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SHOCK INDUCED VAPORIZATION OF ANHYDRITE $CaSO_4$ AND CALCITE $CaCO_3$

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Abstract. Discovery of abundant anhydrite ($CaSO_4$) and gypsum ($CaSO_4.2H_2O$) in the otherwise carbonate sediments comprising the upper portion of the rocks contained within the Chicxulub impact crater has prompted research on the shock-induced vaporization of these minerals. We use a vaporization criterion determined by shock-induced entropy. We reanalyze the shock wave experiments of Yang [1]. He shocked 30% porous anhydrite and 46% porous calcite. Post-shock adiabatic expansion of the sample across a 5 mm-thick gap and then impact upon an aluminum witness plate backed by LiF window that is monitored with a VISAR. Reanalysis uses Herrman's P-α model [2] for porous materials, and a realistic interpolation gas equation-of-state for vaporization products. Derived values of the entropies for incipient and complete vaporization for anhydrite are 1.65±0.12 and 3.17±0.12 kJ(kg.K)$^{-1}$, and for calcite these are 0.99±0.11 and 1.93±0.11 kJ(kg.K)$^{-1}$. Corresponding pressures for incipient and complete vaporization along the Hugoniot of non-porous anhydrite are 32.5 ±2.5 and 122±13 GPa and for non-porous calcite are 17.8 ±2.9 and 54.1±5.3 GPa, respectively. These pressures are a factor of 2-3 lower than reported earlier by Yang.

INTRODUCTION

It is well accepted that the extinction of many marine and terrestrial biota at the K/T boundary is related to the impact on earth by a large bolide at the Chicxulub site [3]. Discovery of about 30% anhydrite and gypsum and about 70% calcite in the upper 3 km layer of the rock at the impact site has prompted active research on these minerals. Following the impact, the decrease in solar insolation introduced by sulfuric acid aerosols formed from the SO_2 and SO_3 (combining with largely impact-in-the-ocean-derived H_2O aerosols) injected into the stratosphere could result in global cooling for about a decade. Subsequent to this temporary cooling, greenhouse warming on a 10^4-10^5 years time scale could have occurred due to injection of CO_2 (shock-induced from vaporization of calcite). Evaluation of the extent of these extinction mechanisms involves the knowledge of the amount of material shock vaporized on the bolide impact. This entails determination of criteria for shock-induced vaporization of anhydrite and calcite.

To determine vaporization criteria for anhydrite and calcite, recently Yang [1] carried out shock wave experiments on porous anhydrite and porous calcite using propellant and light-gas guns at Lindhurst Laboratory. Post-shock adiabatic expansion of the sample across a 5 mm-thick gap and then impact upon an aluminum witness plate backed by LiF window was monitored with a VISAR. The response of anhydrite and calcite was studied by comparing the simulated Al/LiF interface velocity profiles with experimental ones. In the present study, we have reanalyzed the experimental data using vaporization criterion based on shock-generated entropy. Also, improved equations of state of porous materials and vaporized products are employed.

EXPERIMENTS

Yang [1] conducted four shock wave experiments on porous anhydrite samples with density 2.09 ± 0.04 g/cm^3 (porosity 30%) and three experiments on porous calcite samples with density 1.45 ± 0.04 g/cm^3 (porosity 46%). Shock waves were generated in targets by the impact of flyer plates, mounted on the face of the gun-launched projectiles. The target assembly, as shown in Fig. 1, consisted of a driver plate, porous sample, followed by a gap for adiabatic expansion of the shocked sample, an aluminum witness plate, and LiF window. The impact of flyer plate onto the driver plate introduces a shock wave into the driver plate and then into the sample. The shock wave reflects from the free surface of the sample (at the gap) as a rarefaction wave causing adiabatic expansion of the material. The accelerated expanded material impacts the aluminum witness plate inducing shock wave in it and also a backward propagating shock wave in the previously shocked and released material launched at the sample free-surface. The velocity profile at the interface of Al witness plate and LiF window is monitored using a VISAR. More experimental details are found in Yang [1].

ANALYSIS OF EXPERIMENTAL DATA

The analysis has been carried out by performing numerical simulations and comparing the numerically simulated velocity histories of the Al/LiF interface with the experimentally determined histories. Numerical simulations were performed using a one-dimensional Lagrangian finite difference code WONDY [4], which

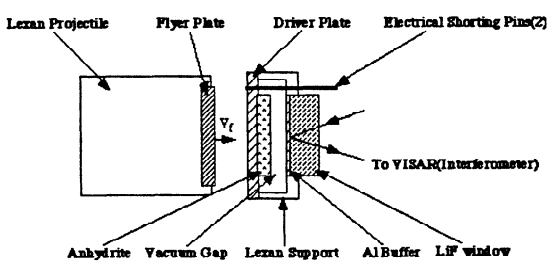

Figure 1. Schematic diagram of the experimental setup.

integrates the equations of conservation of mass, momentum and energy for a wave propagating in a medium. Important features of the present simulations are discussed below.

Vaporization Criterion

Previously, material was assumed to be shock vaporized if the net gain in the internal energy achieved upon shock loading and subsequent release exceeds the energy required to incipiently vaporize at low pressures. Thus, the 'energy criterion', requires the knowledge of both the Hugoniot and a family of release isentropes for unloading from different shock pressures. Because of the paucity of the release adiabat data (e.g., for anhydrite and calcite), the 'energy criterion' for vaporization is subject to many model assumptions. Instead we use 'entropy criterion' for vaporization [5,6]. A material is considered to be vaporized if the entropy gain resulting from a shock compression exceeds the entropy excess needed to vaporize the material at ambient pressure. This assumes that all the entropy gain occurs upon shock compression and the subsequent release is isentropic. As the WONDY code employed for analyses by Yang [1] did not calculate entropy of the shocked material, he used an 'equivalent energy criterion' for vaporization. For the present analysis we revised the WONDY code and now explicitly calculate entropy gain in all materials and employ 'entropy criterion' for vaporization.

The entropy increase upon shock compression has been determined using the relation,

$$\Delta S_H = \Delta S_{tr} + \int_{T_S}^{T_H} \frac{C_v}{T} dT$$

where ΔS_{tr} is the entropy change of phase transition between the initial and the phase into which the sample has been shocked. Thus ΔS_{tr} is zero if there is no phase transition, otherwise it is the entropy of the high pressure phase relative to that of the low pressure phase at room temperature and pressure. T_H and T_S are temperatures along Hugoniot and isentrope at the same compression.

Fig. 2 displays the shock-induced entropy gain for porous and crystal-density anhydrite as well as calcite. As C_v data are not available for anhydrite and calcite, the Dulong-Petit values were used for the present calculations.

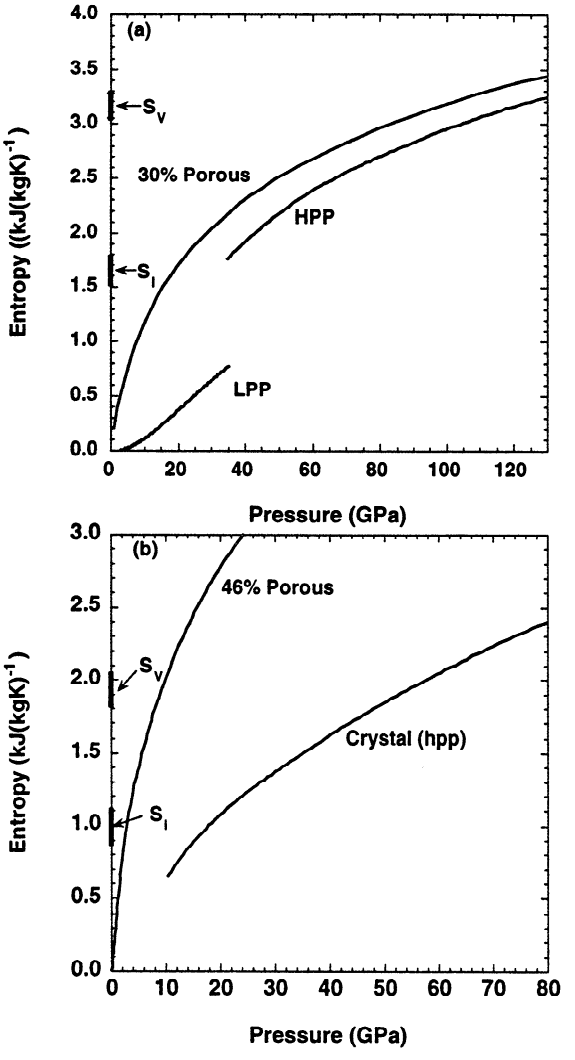

Figure 2. Calculated entropy gain versus shock pressures for porous and crystal-density (a) anhydrite and (b) calcite. S_I and S_V indicate entropy required to initiate and complete vaporization, respectively.

Equation of State

For the porous anhydrite and calcite measured equation of states (eos) are not available. In the present study, we have constructed these eos by using P - α model of Herrmann [2]. This model properly accounts for the irreversible compaction behavior for loading, unloading and reloading of the porous material. We use the Hugoniot eos of the nondistended material as the reference state. The eos of the porous material is described as P = $f(V/\alpha, \varepsilon)$, where P = $f(V_s, \varepsilon)$ is the eos of solid material, $\alpha = V_s/V$, and V_s and V are the specific volumes of solid and porous materials at the same pressure and ε is the specific energy at volume, V. The parameter α is described differently in three different compaction regimes: above certain shock pressure P_s, the pores are assumed to be closed (α = 1); below some elastic pressure, P_e, the change in α is assumed to be equal to that associated with the elastic deformation of pores; for loading between P_s and P_e, the pores are assumed to close irreversibly and the crushing P-α relation is employed. The values of α are constrained to yield continuous values of P at the regime boundaries.

The eos of the vaporized material has the form that is continuous with the Mie-Gruneisen equation at normal solid density but reduces to an ideal gas behavior in the low density expanded state of material.

For the partially vaporized material, pressure has been calculated as

$$P = (1-R_f)\, P_s + R_f\, P_v$$

where P_s and P_e are the pressure determined from the porous solid eos and vapor eos, and R_f is the fraction of the vaporized material given by $R_f=(\Delta S_H-S_I)/(S_V-S_I)$. The method employed for treating the partially vaporized material needs improvement, but it is a good approximation as the pressure and its derivative with respect to density from the eos of solid and vapor are continuous near the normal solid density.

For other target materials, the Mie-Grüneisen eos has been used.

Numerical Simulations and Results

Numerical simulations have been carried out for various values of the entropies of incipient vaporization S_I and complete vaporization S_V starting from the theoretically estimated values. The theoretical estimates were made using available thermodynamical data at normal pressure and high temperatures (Robie et al. [7]). We have determined the values of S_I and S_V from the experimental velocity histories by carrying out numerical simulations and finding out values of S_I and S_V which result in best agreement between the simulated and the experimental profiles (Fig. 3). For anhydrite, the best fitting parameters were obtained by visual comparison of experimental and

calculated wave profiles yielding S_I=1.65±0.12 kJ(kg.K)$^{-1}$ and S_V=3.17±0.12 kJ(kg.K)$^{-1}$. These values are 22% and 15 % less respectively than the theoretical values of 2.12 kJ(kg.K)$^{-1}$and 3.73 kJ(kg.K)$^{-1}$. The pressures of incipient and complete vaporization along Hugoniot for single-crystal anhydrite corresponding to the new entropy values are 32±2.5 GPa and 122±13 GPa, respectively. These values are less than 81±7 GPa and 155±13 GPa reported by Yang [1].

For calcite the values of S_I and S_V are derived to be 0.99±0.11 and 1.93±0.11 kJ(kg.K)$^{-1}$. These values are also smaller than the theoretical estimates of 1.47 and 2.91 kJ(kg.K)$^{-1}$. The pressures of incipient and complete vaporization along Hugoniot for non-porous calcite are found to

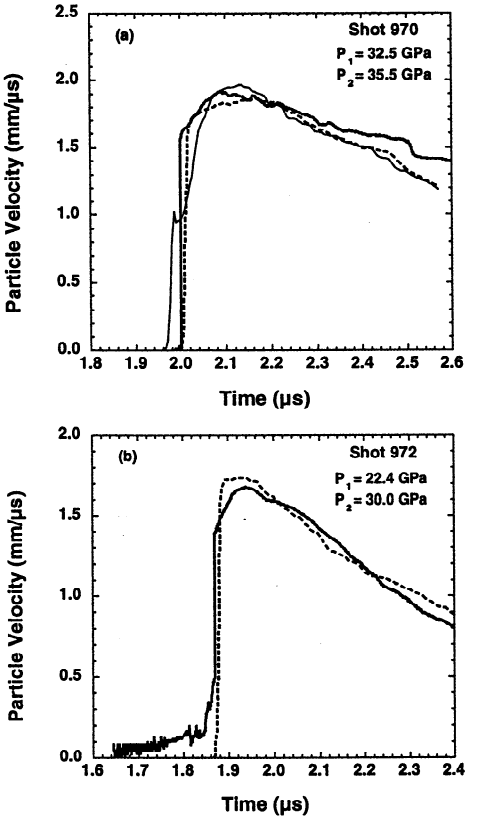

Figure 3. Typical comparison of numerical simulation (dotted line) and experimental result (solid line) for experiments on (a) anhydrite and (b) calcite. Thin curve in (a) displays the results of numerical simulation with theoretical value of S_I and S_V. P_1 and P_2 are the pressures of initial shock and recompression shock, respectively.

Table 1. Summary of results

Quantity	Anhydrite	Calcite
S_I	1.65±0.12 kJ(kg.K)$^{-1}$	0.99±0.11 kJ(kg.K)$^{-1}$
S_V	3.17±0.12 kJ(kg.K)$^{-1}$	1.93±0.11 kJ(kg.K)$^{-1}$
P_I	32.5±2.5 GPa	17.8±2.9 GPa
P_V	122±13 GPa	54.1±5.3 GPa

be 17.8 ±2.9 and 54.1±5.3 GPa, which are also less than 54±6 GPa and 103±12 GPa reported by Yang [1]. The results are summarized in table 1 and displayed in Fig. 2.

CONCLUSIONS

We have reanalyzed the experimental data of Yang [1] on anhydrite and calcite, employing entropy criterion for vaporization during the numerical simulations. The determined Values of the entropy for incipient and complete vaporization for anhydrite are 1.65±0.12 kJ(kg.K)$^{-1}$ and 3.17±0.12 kJ(kg.K)$^{-1}$, and for calcite these are 0.99±0.11 and 1.93±0.11 kJ(kg.K)$^{-1}$. Corresponding pressures for incipient and complete vaporization along the Hugoniot of non-porous anhydrite are 32.5 ±2.5 and 122±13 GPa and for non-porous calcite are 17.8 ±2.9 and 54.1±5.3 GPa, respectively. These pressures are a factor of 2-3 lower than reported earlier by Yang.

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